

Recovery and Distribution of Biosolids-Derived Trace Metals in a Clay Loam Soil

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ABSTRACT

The long-term mobility of trace metals has been cited as a potential hazard by critics of EPA 503 rule governing the land application of biosolids. The objectives of this study were to assess the accumulation of Cu, Ni, Cd, and Zn within the soil profile; the distribution of exchangeable, specifically adsorbed, organic, and oxide fractions of each metal; and mass balance of Cu, Ni, and Zn 17 yr after a single biosolids application. Biosolids were applied to 1.5- × 2.3-m confined plots of a Davidson clay loam (fine, kaolinitic, thermic Rhodic Kandudult) in 1984 at 0, 42, 84, 126, 168, and 210 Mg ha⁻¹. The highest biosolids application supplied 4.5, 750, 43, and 600 kg ha⁻¹ of Cd, Cu, Ni, and Zn, respectively. Soils were sampled to a depth of 0.9 m and sectioned into 5-cm increments after separating the Ap horizon. Total (EPA-3050B), bioavailable (Mehlich-I), sequential extraction, and dispersible clay analyses were performed on samples from the control, 126 Mg ha⁻¹, and 210 Mg ha⁻¹ treatments. Trace metals are still concentrated in the top 0.2 m with slight enrichment down to 0.3 m. More than 85% of applied Cu, Ni, and Zn are still found in the topsoil where biosolids was incorporated and 95% or more of the applied metals were accounted for with mass balance calculations. Mehlich-I results showed a slight increase in metal concentration down to 0.35 m. Biosolids application increased the concentrations of trace metals in all the extracted fractions. The major portions of Cu, Zn, and Ni are associated with the metal-oxides fraction. Dispersible clay content and water-soluble metal contents were low and except for water-soluble Zn they were not affected by biosolids application. Results from this study showed that 17 yr after biosolids application there was negligible movement of trace metals through the soil profile and consequently there is little risk of contamination of ground water at this site.

LAND APPLICATION of biosolids increases metal concentrations in soils (Sloan et al., 1998). The USEPA developed a risk assessment method (USEPA, 1992) to evaluate the potential negative effects of pollutants in biosolids. The USEPA 40 CFR Part 503 was promulgated as the *Standards for the Use and Disposal of Sewage Sludge* (USEPA, 1993). The Part 503 rule permits long-term application of biosolids to agricultural land with the assumption that the soil accumulation of trace metals from biosolids meeting ceiling concentrations will not cause environmental or health hazards during or after the application period.

The protectiveness of the Part 503 rule has been called into question based on assumptions about trace metal immobilization made in the underlying risk assessment

(McBride, 1995; Harrison et al., 1997). The risk assessment assumes that Fe, Al, and Mn oxy-hydroxides and organic matter added to soil along with biosolids increase the soil capacity to adsorb and bind trace metals (Corey et al., 1987). Selective adsorption and precipitation of trace metals on oxide surfaces provide the basis for immobilization in biosolids-amended soils. Inorganic minerals (Fe and Al oxides, silicates, phosphates, and carbonates) may comprise 30 to 60% of digested primary biosolids (Metcalf & Eddy, 1991). The potential for trace metal sorption in biosolids-amended soils is further increased by newly formed oxide precipitates (Corey et al., 1987).

The concept of long-term metal immobilization in soil has been challenged when mass balance calculations at a number of land application studies were unable to account for up to half of biosolids-applied trace metals (Dowdy et al., 1991; Brown et al., 1997; McBride et al., 1997). Researchers reporting such discrepancies have attempted to explain the apparent metal loss as due to leaching (McBride, 1995), dispersion of trace metals due to tillage (McGrath and Lane, 1989), and incomplete chemical extraction from soil or overestimation of trace metals loadings (Dowdy et al., 1991).

Most studies of metal leaching in soil columns (Emmerich et al., 1982; Miller and McFee, 1983) or field investigations (Williams et al., 1984; McGrath and Lane, 1989) conclude that trace metals are strongly bound to topsoil. Other field investigations (Lamy et al., 1993) as well as soil column studies (Frenkel et al., 1997) have documented rapid leaching of significant concentrations of Zn, Cu, Cr, and Cd.

Suspended clay-sized particles may facilitate the transfer of strongly sorbing contaminants, generally regarded as relatively immobile in soil. McBride et al. (1999) observed that Zn, Cd, and Cu in percolates collected at a 60-cm depth in a long-term study are largely in complexed form probably with dissolved organic matter. Correlations have also been found between levels of dissolved organic matter and the concentration of Hg, As, Cu, Cd, Zn, and Cr in leachates (Kalbitz and Wennrich, 1998; McBride et al., 1997). Other research evidence showed enhanced metal mobility associated with water-dispersed colloidal particles moving through soil macropores and fractures (Liang and McCarthy, 1995; Ouyang et al., 1996). Soluble complexing ligands in biosolids cause certain trace metals to be more mobile than they would be in the absence of organics (Frenkel et al., 1997; Camobreco et al., 1996).

Total metal concentration does not furnish sufficient information regarding the potential availability of elements (Srikanth and Reddy, 1991). Trace metals can be associated with various soil fractions, which affect their

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Abbreviations: EPA-3050B, method used to determine total metal concentration.

phytoavailability and mobility in soil. The distribution of various forms of trace metals in soil may also change with time. Metals may accumulate in soil in different proportions as water soluble, exchangeable, and organically bound or be associated with oxides (Salomons and Forstner, 1980). Sequential extraction can be used to characterize the distribution of the different chemical fractions of the trace metals in soil (Berti and Jacobs, 1996).

Long-term annual application of biosolids at rates limited by N and P requirements will cause a gradual increase in the concentration of trace metals in amended soil. Most of the data used to develop USEPA regulations were obtained from studies in which trace element availability was measured during the years of biosolids application. Research on the behavior of trace metals in soils that have approached equilibrium years after biosolids application is needed to understand the long-term effect of biosolids application on agricultural lands. A field test was initiated in 1984 on a highly weathered, deep, well-drained Davidson clay loam soil with controlled lateral flow field experimental plots (Rappaport et al., 1988). These plots received a single application of several rates of biosolids that contained considerably higher concentrations of Cu and Zn than currently found in land-applied biosolids. The rates of the trace metals applied and the experimental plot design provided an opportunity to investigate the fate of trace metals in soil amended with biosolids 17 yr before sampling.

The objectives of this study were to investigate (i) the accumulation of biosolids-applied trace metals by depth; (ii) the distribution of Cu, Cd, Ni, and Zn into soluble and exchangeable, chemisorbed, organically bound, and Fe oxide-bound fractions; and (iii) the percent of applied Cu, Ni, and Zn remaining in the soil 17 yr after biosolids application.

MATERIALS AND METHODS

Background

A field test was established in the spring of 1984 to evaluate the use on cropland of aerobically digested biosolids from a wastewater treatment plant with considerable industrial input (Rappaport et al., 1988). The experiment was conducted at the current site of the Northern Piedmont Agricultural Research and Educational Center (NPAREC) in Orange, Virginia, on a Davidson clay loam. The chemical and physical properties of this piedmont soil when the original biosolids applications treatments were made are presented in Table 1.

Field experimental plots were constructed to prevent the lateral movement of the biosolids. The plots consisted of an isolated volume of soil that measured 2.3 m long \times 1.5 m wide \times 0.9 m high. Isolation of this soil was accomplished by

Table 1. Chemical and physical properties of the Ap horizon of the Davidson clay loam used for the biosolids study in 1984 at the Northern Piedmont Agricultural Research and Educational Center (NPAREC) in Orange, Virginia (Rappaport et al., 1988).

pH	Organic matter g kg ⁻¹	Cation exchange capacity cmol _c kg ⁻¹	Amorphous and crystalline			Particle size distribution		
			Al	Mn	Fe	Sand	Silt	Clay
			g kg ⁻¹					
5.7	18	12.5	4.74	1.28	42.5	153	471	376

Table 2. Properties of the aerobically digested sewage sludge (ADSS) and Part 503 ceiling concentrations (CC) and pollutant concentrations (PC) standards for land-applied biosolids (Rappaport et al., 1988).

Trace metal	ADSS	CC	PC
	mg kg ⁻¹		
Cd	21.5	85	39
Cu	3650	4300	1500
Ni	210	420	420
Pb	640	840	300
Zn	2980	7500	2800

excavating a ditch 20 cm wide and 0.9 m deep around each plot and wrapping the sides of these soil blocks with 254- μ m polyethylene film. Aluminum flashing extended 15 cm above the soil surface to prevent lateral movement and runoff. Eventually, the Al-flashing was replaced by wooden boards 5 cm wide \times 20 cm deep. This setup ensured complete isolation of the plots against lateral movement and so the only possible way of metal movement at the site would be via leaching, soil removal by sampling, or plant uptake. An aerobically digested biosolids was applied by hand at rates of 0, 42, 84, 126, 168, and 210 dry Mg ha⁻¹ in the spring of 1984. Biosolids were incorporated in the Ap (top 14–16 cm) horizon by rototilling. The plots are rototilled every year down to 15 cm. The treatments were arranged in a randomized complete block design with four replicates.

The current ceiling limits (USEPA, 1993) and actual concentration of trace metals found in the biosolids are also shown in Table 2. The biosolids contained considerably higher concentrations of trace metals than are currently found in land-applied biosolids. Copper, Zn, and Pb concentrations were above the pollutant concentrations standard, while Cd and Ni were lower than the pollutant concentrations; thus, USEPA regulations would require lifetime loading rates of this biosolids to be tracked. The 210 Mg ha⁻¹ biosolids rate supplied 4.5 kg Cd, 750 kg Cu, 43 kg Ni, and 600 kg Zn ha⁻¹ (Table 3). These amounts are below the maximum cumulative pollutant loading rate application of trace metals that can be applied to soils in biosolids that meets ceiling concentrations. This rate provided 12% of the Cd, 50% of the Cu, 10% of the Ni, and 21% of the Zn permitted loadings.

Plot Management

The experimental plots were annually planted to 'Pioneer 3193' field corn (*Zea mays* L.) from 1984 to 2000. Agronomic practices, seedbed preparation, pest control, and weeding were performed according to Virginia Cooperative Extension recommendations (Brann and Mullins, 2000). Soil fertility requirements were met by applying fertilizer N, P, and K according to Virginia Tech Soil Testing Laboratory recommendations (Donohue and Heckendorn, 1994). The aboveground portion of the crop was totally removed at physiological maturity. Lime (CaCO₃) applications in 1989 and 1997 were made to raise the pH to 6. The average pH was 5.8 and 5.6 in 2001 and 2002, respectively.

Soil Sampling and Processing

Soil cores were sampled from the 0, 126, and 210 Mg ha⁻¹ treatment plots on 19 June 2001. Four 3.5-cm-diameter cores were collected in plastic sleeves to a depth of 0.9 m using a Giddings (Windsor, CO) hydraulic soil probe. After removing the cores, sodium bentonite was added to the holes to fill the lower 75 cm. The top 15 cm was filled with topsoil from the same plot.

The cores were kept intact in plastic tubes until they were

Table 3. Quantity of biosolids, trace metals, and total N and P applied at the Northern Piedmont Agricultural Research and Educational Center (NPAREC) in Orange, Virginia (Rappaport et al., 1988).

Biosolids application	Macronutrients		Trace metals			
	N	P	Cd	Cu	Ni	Zn
Mg ha ⁻¹			kg ha ⁻¹			
42	670	1380	0.9	153	8.6	125
84	1340	2760	1.8	304	17.2	248
126	2010	4140	2.7	456	25.8	372
168	2680	5520	3.6	608	34.4	496
210	3350	6900	4.5	760	43.0	620
CPLR†			39	1500	420	2800

† Cumulative pollutant loading rate allowed by USEPA regulation.

sectioned by depth at 5-cm intervals after the Ap horizon (top 15 cm) had been separated in the laboratory. Samples were labeled, air-dried in clean plastic bags, and ground with a glass mortar and pestle to pass a 2-mm sieve.

Metal Analysis

Several digestion and extraction methods were employed for metal analysis. Trace metals were extracted by the Mehlich-I, EPA-3050B, and EPA-3052 methods and fractionation was accomplished with sequential extractions. The Mehlich-I method (Mehlich, 1953) uses a solution of 0.05 M HCl and 0.0125 H₂SO₄ to extract a fraction that is an indicator of plant-available soil trace metals. The EPA-3050B (USEPA, 1996a) method is a strong acid digestion procedure that extracts all elements that could become "environmentally available." The method extracts 75% to 90% of the total metal. It is not designed to extract elements bound within the silicate structure. The procedure utilizes a mixture of HCl, HNO₃, and H₂O₂ with supplemental heating to extract trace metals. Metal concentrations were determined using Thermo Jarrell Ash ICAP (inductively coupled plasma-atomic emission spectrometry; ICP-AES) (Thermo Electron, Waltham, MA). The EPA 3052 (USEPA, 1996b) microwave digestion procedure was employed to determine total metal concentrations for mass balance estimation. Microwave methods are known to be rapid and give reproducible recovery with better precision than conventional hot plate digestion procedures (Millward and Kluckner, 1989). Briefly, a 0.5-g aliquot of sieved air-dried soil was mixed with 9 mL HNO₃, 2 mL HF, and 3 mL HCl. Temperature of the mixture was raised to 140°C in 6 min and maintained at 140°C for an additional 9 min. Metal concentration was determined using a PerkinElmer (Wellesley, MA) Model 3300 atomic absorption spectrometer (AAS).

Fractionation

The distribution of Cu, Ni, Cd, and Zn within soluble + exchangeable, specifically sorbed, organically bound, and metal oxide fractions was measured in soil samples taken from the Ap horizon (0- to 15-cm depth) as described by Miller et al. (1986). The procedure consisted of sequential extraction with 0.5 M Ca(NO₃)₂ (exchangeable), Pb(NO₃)₂ (specifically sorbed), 0.1 M K₄P₂O₇ (organic), and oxalate reagent [0.175 M (NH₄)₂C₂O₄ + 0.1 H₂C₂O₄] under UV irradiation (oxide). Calibration blanks were routinely included in the analysis. Metal concentrations were determined using ICP-AES.

Dispersible Clay

Samples from the control, medium (126 kg ha⁻¹), and high (210 kg ha⁻¹) sludge application rates were analyzed for dissolved organic carbon, dispersible clay, and water-soluble trace

metals in the manner described in Southern Cooperative Series Bulletin (1998). Five-gram samples were weighed into a centrifuge tube to which 50 mL of deionized water was added. After shaking for 14 h on a reciprocal shaker, each suspension was allowed to settle undisturbed for 2 h. The dispersed colloidal fraction was sampled from the top 2.5 cm. The aliquot was then oven-dried at 110°C in preweighed Al-boats and the dispersible clay quantified. The remaining suspension in each tube was then filtered (0.2-μm pore size polycarbonate membrane filter). The filtrate was analyzed for water-soluble trace metals using ICP-AES.

Mass Balance

Trace metal recovery was calculated from metals determined in harvested crops for the duration of the study and total metals content in the upper 25 cm of the soil profile. Available data on crop yield and metal uptake compiled for the period 1985 to 2003 were used to estimate metal removal. Whenever data for either yield or uptake were missing, averages for the duration of the study were used. Average crop removal was estimated by multiplying the metal concentration (mg kg⁻¹) by total yield (kg plot⁻¹). The plant metal contents of the control plots were subtracted from each treatment to give the average net uptake per treatment. Averages over the years were added and the net total crop removal was estimated.

Soil bulk density was determined for each soil section. Each section (3.5-cm-diameter × 5-cm-high cylinder) was weighed, and its density calculated to estimate total soil mass. The average bulk density of the Ap horizon was 1.52 g cm⁻³. For the second and third sections, average bulk density was 1.58 g cm⁻³. An estimated 30 kg of the Ap section of each plot was lost to annual sampling and a greenhouse pot experiment. This was included as sampling removal in the mass balance calculation.

Total soil mass of each section was multiplied by its respective metal concentration. The control for each depth was subtracted and the concentrations of each depth increment comprising the 0- to 25-cm soil depth were added. This total content was divided by metal loading in the biosolids to calculate recovery of the biosolids applied trace metals. Total metal concentrations for mass balance estimation were determined using the EPA 3052 microwave digestion procedure. The solutions were then filtered and metal concentrations were determined by AAS.

Statistical Analysis

Two cores per replicate were used for analysis; therefore, all data are averages of eight samples (four replicates per treatment × two samples per replicate). The statistical analysis was performed with the SAS package Version 8.2 for Windows (SAS Institute, 2002). Data were evaluated by analysis of variance (ANOVA) with subsampling and by the least significant difference (LSD) mean separation procedures at the 0.05 level of significance (Steel and Torrie, 1980).

RESULTS AND DISCUSSION

Vertical Translocation of Trace Metals

EPA-3050B

Soil profile total metal (EPA-3050B) concentration data from the same treatments showed an increase in Cu, Zn, and Ni in the Ap horizon with increasing biosolids rate (Fig. 1). Copper, Ni, and Zn concentrations in-

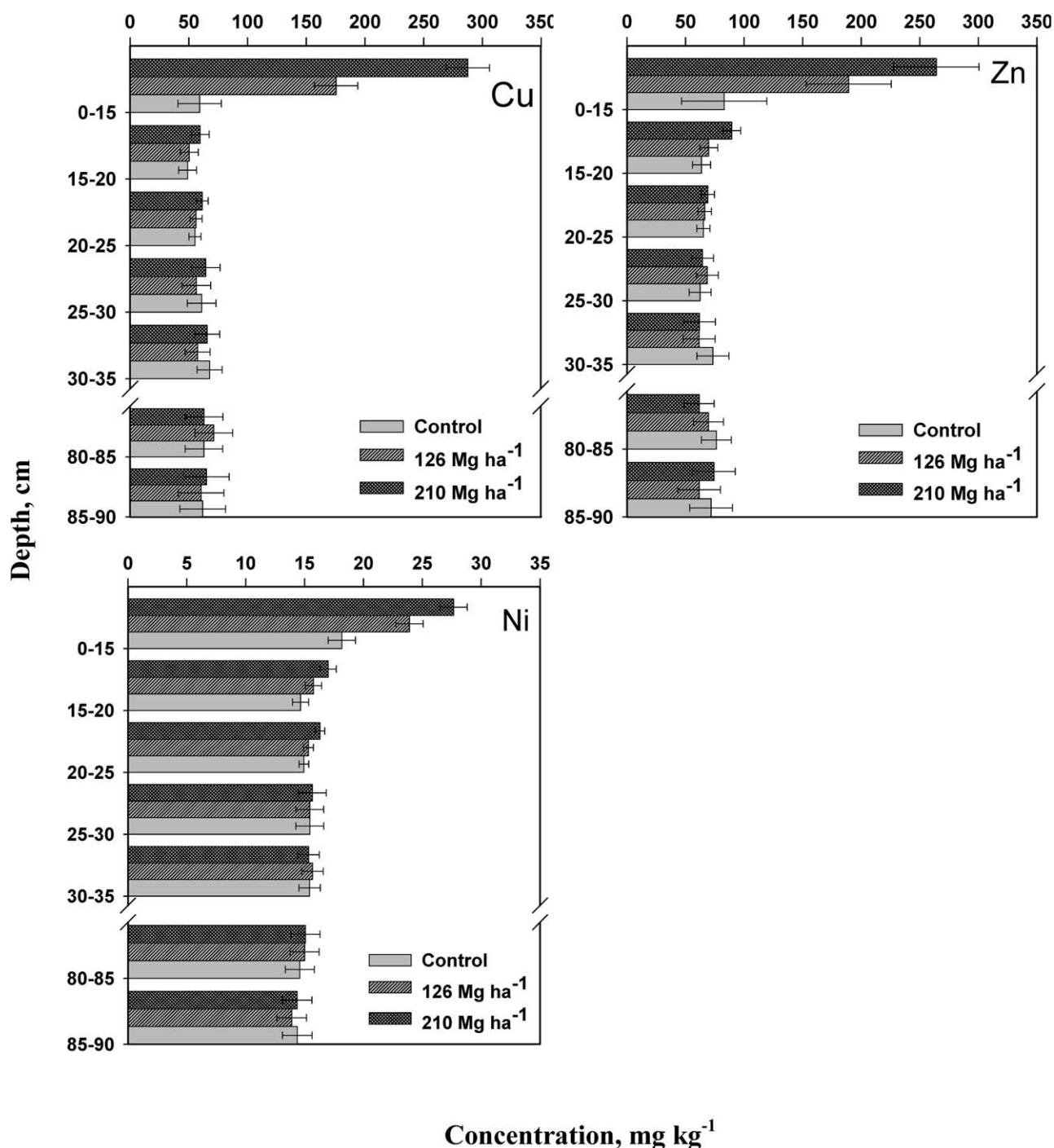


Fig. 1. Distribution of EPA-3050 extractable Cu, Zn, and Ni with soil depth 17 yr after biosolids application. Error bars represent least significant difference.

creased from 60, 18, and 83 mg kg⁻¹ in the control to 287, 28, and 264 mg kg⁻¹, respectively, in the plots receiving the highest biosolids application rate. This increase reflected the composition of the biosolids applied to the plots. The biosolids-applied metals were still concentrated in the top 20 cm (5 cm below Ap horizon) of the soil profile with minor enrichment down to 25 cm seventeen years after the application of biosolids. At 0 to 10 cm below the Ap there were no significant ($P <$

0.05) differences between the medium and high biosolids treatments. Both were significantly higher than the control. There was no apparent movement of total Cu, Ni, and Zn below this depth.

The apparent lack of trace metals leaching is consistent with the results of other studies. Barbarick et al. (1998) reported no leaching below the plow layer of trace metals, except Zn from five or six biosolids applied during an 11-yr period. Chang et al. (1983) determined

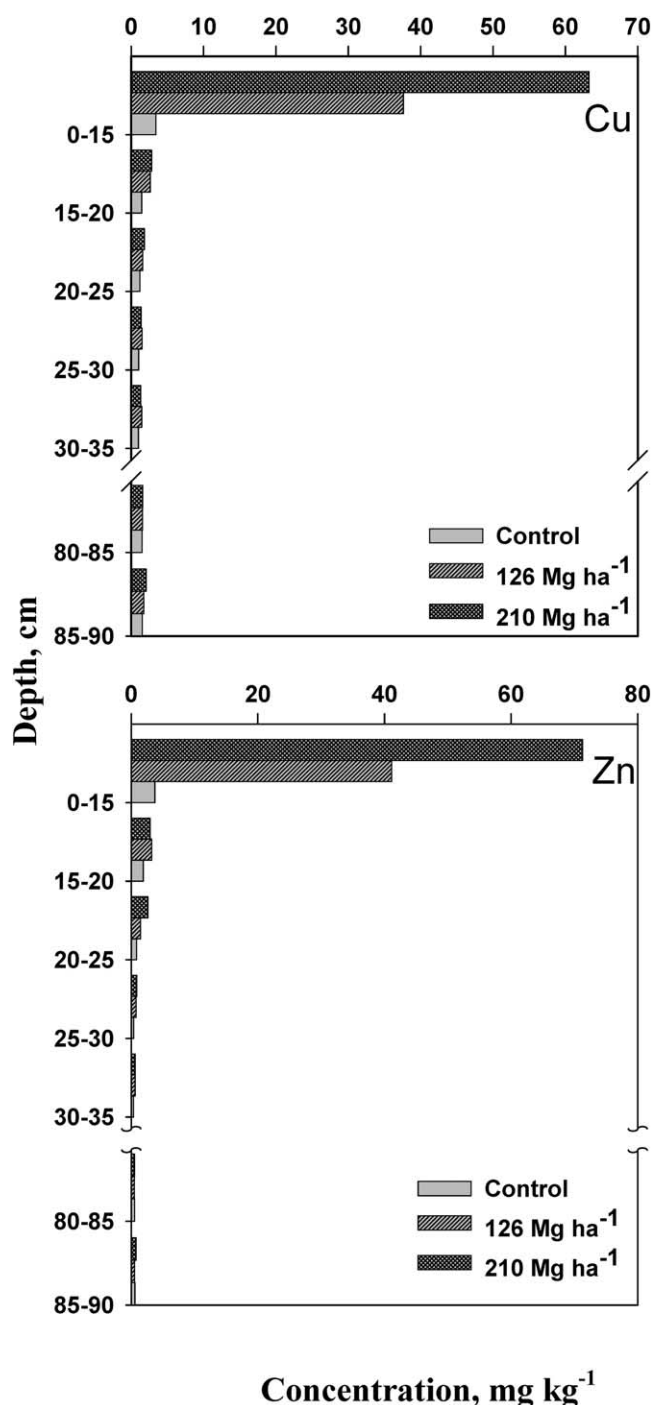


Fig. 2. Distribution of Mehlich-I extractable Cu and Zn with soil depth 17 yr after biosolids application.

that more than 90% of Cd and Zn was concentrated in the topsoil (0–15 cm) after six consecutive biosolids applications at an annual rate of 90 Mg ha⁻¹.

Most studies reported the accumulation of trace metals in the zone of incorporation with minimal movement below the root zone (Berti and Jacobs, 1998; Chang et al., 1983; McGrath and Lane, 1989; Brown et al., 1997; Sloan et al., 1997). Generally, researchers concluded that trace metals were still largely concentrated in the

Table 4. Distribution of dispersible clay content by depth and biosolids application rate.

Depth	Dispersible clay content		
	Control	126 kg ha ⁻¹	210 kg ha ⁻¹
cm	g kg ⁻¹		
0–15	13.5a†	12.8a	12.6a
15–20	12.1a	12.0a	12.3a
20–25	6.20a	5.70a	6.02a
25–30	0.50a	0.55a	0.50a

† Row means for each treatment followed by different letters are significantly ($P = 0.05$) different.

topsoil. An exception was noted by Robertson et al. (1982) who measured the movement of some trace metals to a depth of 0.4 to 0.6 m when liquid biosolids was applied at high rates to three sand Ultisols of Florida.

Mehlich-I

Soil profile Mehlich-I extractable Cu and Zn concentrations in the Ap horizon (0–15 cm) increased with biosolids rate. At the highest biosolids input rate (210 Mg ha⁻¹) the Cu and Zn concentration in the 0- to 15-cm depth increased from 3.4 and 3.7 mg kg⁻¹ to 63 and 71 mg kg⁻¹, respectively. Metal movement occurred beyond the top horizon sampled. Slight enrichment in metal concentration was observed to a depth of 20 cm below the Ap. No significant movement was detected below this depth (Fig. 2). At the 0- to 20-cm soil depth below the Ap horizon the concentration of Cu and Zn in the treated soil were significantly ($P < 0.05$) higher than the control, but there were no significant differences in metal concentrations between the medium and high treatments plots.

Dispersible Clay

Suspended clay-sized particles may facilitate the transfer of contaminants through soil. Recent evidence showed enhanced metal mobility associated with water-dispersed colloidal particles moving through soil macropores and fractures in some studies (Liang and McCarthy, 1995; Ouyang et al., 1996). In the present study, there were no significant effects of biosolids application on dispersible clay content in the top 30 cm (Table 4). The amount of dispersible clays was low. It was highest in the 0- to 15- and 15- to 20-cm sections but dropped sharply at lower depth.

Karathanasis (1999) found that soil with low negative surface charge, large particle size, and high Fe- and Al-hydroxyoxides contents had the lowest metal colloid-mediated transport potential as compared with soils with high negative surface charge and organic carbon concentration. The Davidson soil is high in Al- and Fe-oxides and has a moderate charge, which might explain the low dispersible clay content (especially in the deeper horizons). The total metal concentration of Cu, Cd, and Zn associated with the dispersible clay fraction in the Ap horizon increased significantly as biosolids rates increased (Table 5).

The water-soluble Zn concentration increased in the first (0–15 cm) and the second (15–20 cm) layers only,

Table 5. Total metal concentration of dispersible clay fraction in top 15 cm as determined by EPA-3050B.

Treatment	Cu	Zn	Cd	Ni
kg ha ⁻¹	mg kg ⁻¹			
0 (Control)	87.6c†	144c	2.29b	30.9
126	196b	223b	2.61b	34.3
210	252a	293a	3.20a	39.2

† Column means for each treatment followed by different letters are significantly ($P = 0.05$) different.

where biosolids loading increased. No significant differences were observed below this depth (Table 6). Data on water-soluble Cu were inconclusive because the concentrations of many samples were below the detection limit. These results strengthen our finding of limited metal movement through the soil profile. The potential for metal migration at this site at the current conditions appears to be very low.

Fractionation

Sequential extraction procedures have been used to determine the amounts and proportions of trace metals present in different soil fractions (Shuman, 1991). Fractionation can provide useful information regarding the distribution of the trace metals in question, the affinity of trace metals for different soil components, and the potential mobility of trace metals under prevailing conditions. Interpretation of sequential extraction results should be made with caution because the sequence of extraction may affect the concentration of metals in each fraction, and the nonspecificity of the extractants may not provide accurate absolute concentrations of the metals in each fraction (Miller and McFee, 1983; Miller et al., 1986; Ahnstrom and Parker, 1999).

Biosolids application significantly ($P < 0.001$) increased the Zn concentration in each of the four fractions examined in the Ap horizon (Table 7). Zinc concentrations increased from 1.0, 3.1, 26, and 1.4 mg kg⁻¹ to 35, 45, 86, and 18.6 mg kg⁻¹ in the exchangeable, specifically adsorbed, metal-oxide, and organic fractions, respectively, with the highest biosolids application rate. The greatest percentage increase in Zn was observed in the exchangeable and specifically adsorbed fractions; however, the metal-oxide fraction had the highest Zn concentration in all treatments. Other researchers reported similar patterns of Zn fractionation in biosolids-amended soils (McGrath and Cegarra, 1992; Sloan et al., 1997; Berti and Jacobs, 1996).

Table 7. Distribution of trace elements among exchangeable, specifically sorbed, metal oxide, and organic fractions in the Ap horizon (0- to 15-cm depth) as determined by sequential extraction.

Fraction	Control	126 kg ha ⁻¹	210 kg ha ⁻¹	Control	126 kg ha ⁻¹	210 kg ha ⁻¹
	Cu			Zn		
Exchangeable	0.24c†	2.0b	7.40a	1.04c	14.3b	34.9a
Specifically sorbed	2.90c	33.6b	62.4a	3.07c	26.3b	45.2a
Oxide	27.7c	80.3b	126a	25.9c	57.6b	86.1a
Organic	4.65c	29.8b	47.9a	1.35c	11.4b	18.6a
	Cd			Ni		
Exchangeable	ND‡	0.98	1.32	ND	ND	0.53
Specifically sorbed	0.43b	0.60ab	0.66a	ND	ND	1.75
Oxide	ND	ND	ND	5.25b	10.5a	12.3a
Organic	ND	ND	ND	ND	ND	ND

† Row means for each treatment followed by different letters are significantly ($P < 0.05$) different.

‡ Not detectable; concentrations were below analytical detection limits, 0.012 and 0.0023 mg L⁻¹ for Ni and Cd, respectively.

Table 6. Water-soluble concentrations of Cu and Zn in the top 30 cm of the soil profile as influenced by biosolids application rate.

Depth	Control		126 kg ha ⁻¹		210 kg ha ⁻¹	
	Cu	Zn	Cu	Zn	Cu	Zn
cm	mg kg ⁻¹					
0–15 (Ap horizon)	0.05	1.50b†	0.02	2.20a	0.05	2.12a
15–20	0.02‡	1.25b	0.05§	1.32b	0.10§	2.68a
20–25	0.02‡	1.74	0.02§	1.83	0.02§	1.95
25–30	0.09	1.86	0.05	1.71	0.04	1.79

† Rows means for each treatment followed by different letters are significantly ($P = 0.05$) different.

‡ Detected in one sample only.

§ Values are the averages of two samples.

The Cu concentrations increased in all four fractions in the Ap soils (Table 7). The highest application rate increased Cu concentrations significantly ($P < 0.001$) from 0.2, 2.9, 27.7, and 4.6 mg kg⁻¹ to 7.4, 62.4, 125.7, and 48 mg kg⁻¹ in the exchangeable, specifically adsorbed, oxide, and organic fractions, respectively (Table 7). The greatest percent increase was found in the specifically adsorbed and organic fractions. The metal-oxide fraction still contained the highest concentration of Cu among all determined fractions. Although strong organic complexes are known to form with Cu, our results indicated that the metal-oxide fraction appears more important in controlling Cu concentration. These results support the finding of other researchers (Sloan et al., 1997).

The concentrations of Cd and Ni applied to these plots were initially low. Cadmium was only detected in the exchangeable and specifically adsorbed fractions, forms that are readily bioavailable (Table 7). Biosolids application increased the concentration of Cd in exchangeable and specifically adsorbed fractions. Soil Cd has been found predominantly in the soluble and exchangeable fractions (Ramos et al., 1994; Wasay et al., 1998). Soil Ni concentrations increased only in the oxide fraction at the 126 and 210 Mg ha⁻¹ treatment and in the exchangeable and specifically adsorbed fractions at the high application rate (Table 7). Nickel concentrations in the other fractions were below the detection limits of the ICP. The concentration of Ni in the metal oxide fraction increased from 5 to 12 mg kg⁻¹ at the highest application rate. Sloan et al. (1997) also reported the greatest increase in Ni concentration in the metal oxide fraction. Berti and Jacobs (1996) found Ni in all soil fractions but predominantly prevalent in the acid soluble and Fe oxide fraction regardless of the total concentration in soils.

Metal Recovery

Incomplete metal recovery has been reported in many biosolids land application studies (Dowdy et al., 1991; Brown et al., 1997). The apparent metal loss was attributed to leaching (McBride, 1995), dispersion of trace metals due to tillage (McGrath and Lane, 1989; Li and Corey, 1993), incomplete chemical extraction from soil (Dowdy et al., 1991), and overestimation of trace metals loadings and bulk density estimation. This illustrates the difficulty of accounting completely for the elements applied. Improved recovery may be possible if the plots are well protected against soil loss and lateral dispersion and when strong acid digestion methods are used to extract most of the total trace metals from soil as was done in this study.

Uptake of trace metals by crops usually represents a small proportion (0.5–1%) of the biosolids-applied metals (McGrath, 1987). Elements removed through plant harvest are not considered a major factor affecting recovery calculation. Our analysis of data on plant yield and metal uptake on these plots supported McGrath's conclusion for Zn. Crop removal accounted for no more than 1.1 and 0.52% for the 126 and 210 Mg ha⁻¹ application rates, respectively (Table 8). Copper uptake accounted for a much lower percentage (0.07%) of the applied Cu.

Significant enrichment of trace metals occurred in the top 25 cm and, therefore, Cu, Ni, and Zn extracted from this soil depth were used in the mass balance calculation. In general, approximately 85% of the applied Cu and Ni and more than 75% of the applied Zn are still present in the zone of incorporation (0–15 cm). When metal concentration in the 15- to 25-cm depth was included in the analysis, approximately 90% of the applied Cu and Ni and more than 85% of Zn were recovered (Table 8). Twice as much Zn as Cu was recovered in the 15- to 25-cm depth. This might be explained by the higher mobility of Zn as shown by the fractionation results and water-soluble concentrations. Seventeen years after biosolids was applied to these plots, approximately 90% of Cu, Ni, and Zn were still concentrated in the top 25 cm. This indicates that Cu, Ni, and Zn moved slowly down the soil profile and, as a result, we conclude that the risk of metal leaching and ground water contamination at this site is low. Similar findings

were reported by other researchers (Chang et al., 1983; Sloan et al., 1997).

CONCLUSIONS

Soil was sampled with depth 17 yr after a one-time biosolids application. The biosolids-applied trace metals were primarily concentrated in the Ap (0–15 cm). Slight enrichment of metals was observed down to 15 cm below the Ap with no apparent movement below that depth. Close to 90% of the applied trace metals Cu, Ni, and Zn were recovered in the top 25 cm and 95% or more of the applied metals were accounted for with mass balance calculations that also included plant uptake and soil removal. The lack of any indication of trace metal movement through the soil profile and the low dispersible clay content lead us to conclude that deviation of recoveries from 100% is more likely due to inherent variance in sampling, extraction, and analytical techniques as well as the possibility of overestimation of trace metals loadings. Leaching of trace metals down the soil profile as well as their removal by crops do not appear to be significant routes of metal loss from this site. Availability of trace metals was significantly greater in soils that received biosolids application. Mehlich-I extractable trace metals were much higher in biosolids-treated soils than the control.

The Davidson soil series consists of a deep, well-drained, moderately permeable soil that is high in clay and sesquioxides. The major portion of the applied trace metals was found in oxides and specifically sorbed fractions. Some Cd and Zn were present in the exchangeable fractions and some Cu in the organic fraction. Water dispersible clay content was low particularly below the surface horizon. The only remaining mechanism for metal movement would be solution percolation and sorption will still dominate at lower depths. Most of the applied Cu, Ni, and Zn are still present in the top 25 cm indicating that movement of Cu, Ni, and Zn at this site is extremely slow. Consequently, this indicates to us that there is a little risk of downward movement and contamination of ground water at this site and for soil with similar conditions and management history.

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Table 8. Mass balance of Cu and Zn detectable at selected soil depths 17 yr after biosolids application.

	Cu		Ni		Zn	
	kg ha ⁻¹	fraction†	kg ha ⁻¹	fraction	kg ha ⁻¹	fraction
126 kg ha ⁻¹ treatment						
0–15 cm	395	0.87	21.2	0.82	304	0.82
15–25 cm	20	0.04	2.8	0.11	28	0.07
Net plant removal	0.39	0.0008	ND‡	ND	4.25	0.01
Sampling removal	18.7	0.04	0.8	0.03	13.6	0.04
Total	434	0.95	24.8	0.96	350	0.94
210 kg ha ⁻¹ treatment						
0–15 cm	679	0.89	40.2	0.93	493	0.8
15–25 cm	26	0.04	5.7	0.14	56	0.09
Net plant removal	0.49	0.0007	ND‡	ND	3.32	0.005
Sampling removal	32.7	0.04	1.48	0.03	22.6	0.04
Total	738	0.97	47.4	1.1	575	0.93

† Recovered fraction of biosolids metals applied.

‡ Not determined. Data on Ni uptake in crops are not available.

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